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High Quality Single Atomic Layer Deposition of Hexagonal Boron Nitride on Single Crystalline Rh(111) Four-Inch Wafers

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The setup of an apparatus for chemical vapor deposition (CVD) of hexagonal boron nitride (*h*-BN) and its characterization on 4 inch wafers in ultra high vacuum (UHV) environment is reported. It provides well-controlled preparation conditions, such as oxygen and argon plasma assisted cleaning and high temperature annealing. In-situ characterization of a wafer is accomplished with target current spectroscopy. A piezo motor driven x-y stage allows measurements with a step size of 1 nm on the complete wafer. To benchmark the system performance, we investigated the growth of single layer *h*-BN on epitaxial Rh(111) thin films. A thorough analysis of the wafer was performed after cutting in atmosphere by methods, including low energy electron diffraction, scanning tunneling microscopy, ultra-violet and X-ray photoelectron spectroscopy. The apparatus is located in a clean room environment and delivers high quality single layers of *h*-BN and thus grants access to inexpensive and large area UHV processed surfaces, which had been restricted to expensive, small area single crystals. The facility is versatile enough for customization to other UHV/CVD processes, e.g. graphene on 4 inch wafers.

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I. INTRODUCTION

Single layer hexagonal boron nitride (*h*-BN) consists of sp^2 hybridized boron and nitrogen and forms sheets, similar to graphene. The rapidly growing interest in *h*-BN is based on its recent exploitation as substrate for graphene devices¹. Besides its usage as insulator or ultra thin dielectric, it might be used for many other applications such as simple lubricant or as a far-ultraviolet fluorescent material².

In order to fully exploit its potential, *h*-BN has to be produced at large scales and in highest quality. To overcome the scalability problem of the exfoliation process from bulk crystals, chemical vapor deposition (CVD) techniques have been successfully applied on polycrystalline Cu foils³. This procedure is in analogy to the one reported for large scale graphene synthesis⁴. In order to achieve highest quality single atomic layers, ultra high vacuum (UHV) CVD preparations on various single crystalline transition metal substrates are well established^{5,6}. Here, we present an apparatus, which combines large area CVD preparations with the high quality achieved by UHV and single crystalline samples. As single crystalline substrates were employed rhodium(111) 4" thin film wafers⁷.

II. LABORATORY INFRASTRUCTURE

An overview of the laboratory installations is given in Figure 1. The UHV chamber is set up within a clean room, which satisfies clean room class requirements ISO 8, according to ISO 14644-1. To further minimize environmental sample contamination, the entry lock chamber can only be accessed via an additional laminar flow box with a High Efficiency Particulate Airfilter (LogicAir, Switzerland).

The UHV system consists of three chambers: An entry lock, a preparation and an analysis chamber. Each chamber has its own ion or turbo molecular pump and may be isolated with UHV valves. The base pressure in the analysis and preparation chambers is $1 \cdot 10^{-10}$ mbar.

The entry lock provides fast sample access, sample storage, plasma cleaning and wafer-scale ion sputtering. O_2 and Ar plasmas are created with an inductively coupled plasma generator (Harrick, USA), which is mounted on top of the chamber. For sputtering, the target can be biased up to 1 kV. To ensure a homogeneous ion impact distribution, the acceleration voltage is directly applied on the wafer, the plasma generator aperture size is

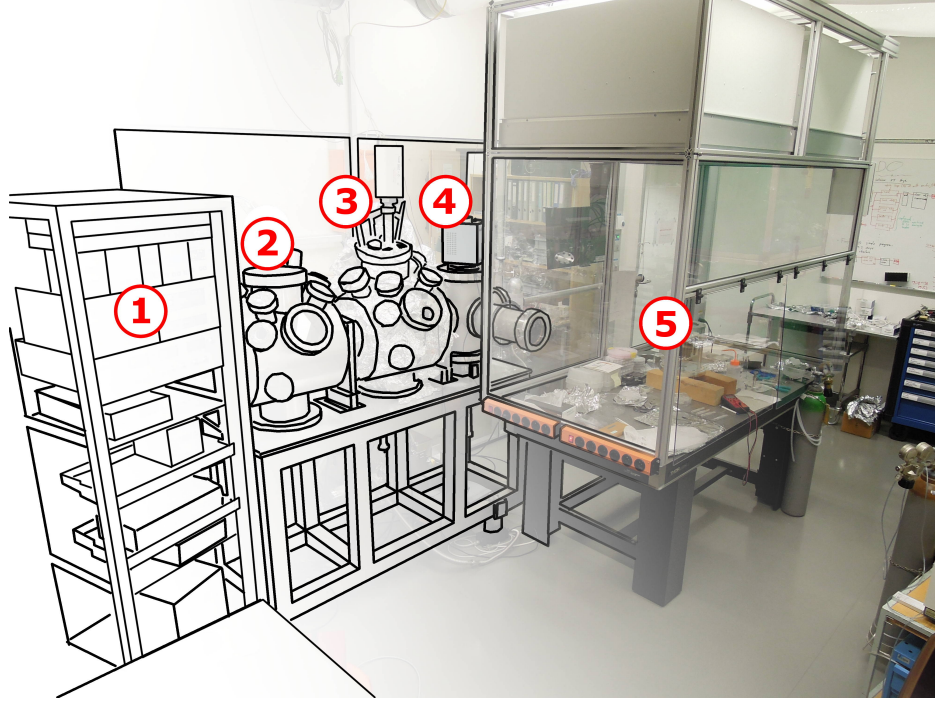


FIG. 1. Schematic view of the laboratory equipment. (1) Infrastructure rack; (2) Analysis chamber; (3) Preparation chamber with mass spectrometer; (4) Fast entry lock with O_2 plasma cleaner and Ar^+ ion sputtering; (5) Laminar flow unit with access to entry lock and optical table with in air experimental set up. The complete apparatus is located in a clean room which complies with ISO 7 clean room class requirements.

70 mm in diameter and its distance to the sample is 230 mm. XPS measurements after sputtering confirm the cleanliness of the sample, neither Si from the plasma tube nor Fe from the aperture are detected on the surface. Ion sputtering currents of a few mA can be reached and adjusted by gas pressure, radio frequency field and acceleration voltage.

The preparation chamber is equipped with a resistive boraelectric heater (Momentum Performance Materials, USA), two leak valves for a CVD preparation and spare flanges for the implementation of additional instrumentation. One of the leak valves is connected to an oxygen gas line for sample cleaning. The other valve has a connection to a glass container in a copper tube, which is temperature stabilized by a water cooled Peltier element. The lowest temperature reached within the glass container is -10°C , which allows for the storage and handling of unstable chemicals, such as borazine $(\text{HBNH})_3$ –the precursor for the *h*-BN preparation. To minimize the warming up of the chamber during preparation, the 4 inch

heater is shielded with Mo foils and placed on a water-cooled copper heat sink. The wafers are annealed by radiative heating with a heater to wafer distance of 16 mm. At a preparation temperature of 820°C, the pressure increases to 3×10^{-9} mbar and the 0.5 mm thick 4" Si-wafer with a 150 nm Rh thin film shows a center-to-edge temperature gradient of 40°C. Sample temperature measurements are realized with pyrometers, which were calibrated to a thermocouple reading in another UHV system. Additional control of the heater is achieved by thermocouples, which are mounted between heater and heat sink.

The analysis chamber is equipped with a two-axis x-y stage, which is driven by piezo motors (SmarAct, Germany) and which allows to scan the wafer with nanometer precision. An electron source (PSP Vacuum Technology, U.K.) is mounted above the sample to perform normal incidence target current spectroscopy (TCS) measurements⁸. The electron source provides an electron beam up to an energy of 100 eV with 250 meV FWHM. The sample current versus incident electron energy spectra are recorded with a source-measure unit (Keithley, USA). The incident kinetic electron energy E_{kin} on the sample is $E_{\text{kin}} = eU_{\text{gun}} + \Phi_{\text{gun}} - eU_{\text{bias}} - \Phi_{\text{s}}$. The current cut off at $E_{\text{kin}} = 0$ is thus determined by the fixed source parameters U_{gun} and Φ_{gun} , the work function of the sample Φ_{s} and the sample bias U_{bias} . Figure 2 shows an overview of the measurement scheme and its capabilities in combination with the x-y stage. At low incident electron energies, the work function Φ_{s} of the wafer sample can be determined relative to the source. For kinetic energies up to $2\Phi_{\text{s}}$ the electron reflectivity ($1 - \frac{I}{I_0}$) of the sample is probed, whereas at higher energies a single electron may cause multiple electron emission, which adds to the reflected electron current. In particular, the sample current may vanish for a given kinetic energy of the electrons. The electron energy is scanned with the sample bias, which requires a flat sample and a minimal magnetic field distortion. But it allows to keep the source current (I_0) constant at any electron energy and the electron absorption (I/I_0) may be determined. Figure 2 c) shows a spatially resolved electron absorption map I/I_0 for 5 eV electrons. The UHV analysis chamber is extendable with additional or different characterization instrumentation.

III. CVD GROWTH OF *H*-BN/RH(111) ON 4" SUBSTRATES

The performance of the CVD preparation capabilities was demonstrated by growing a monolayer of *h*-BN on Rh(111). The boron nitride layer forms in a self-terminating process

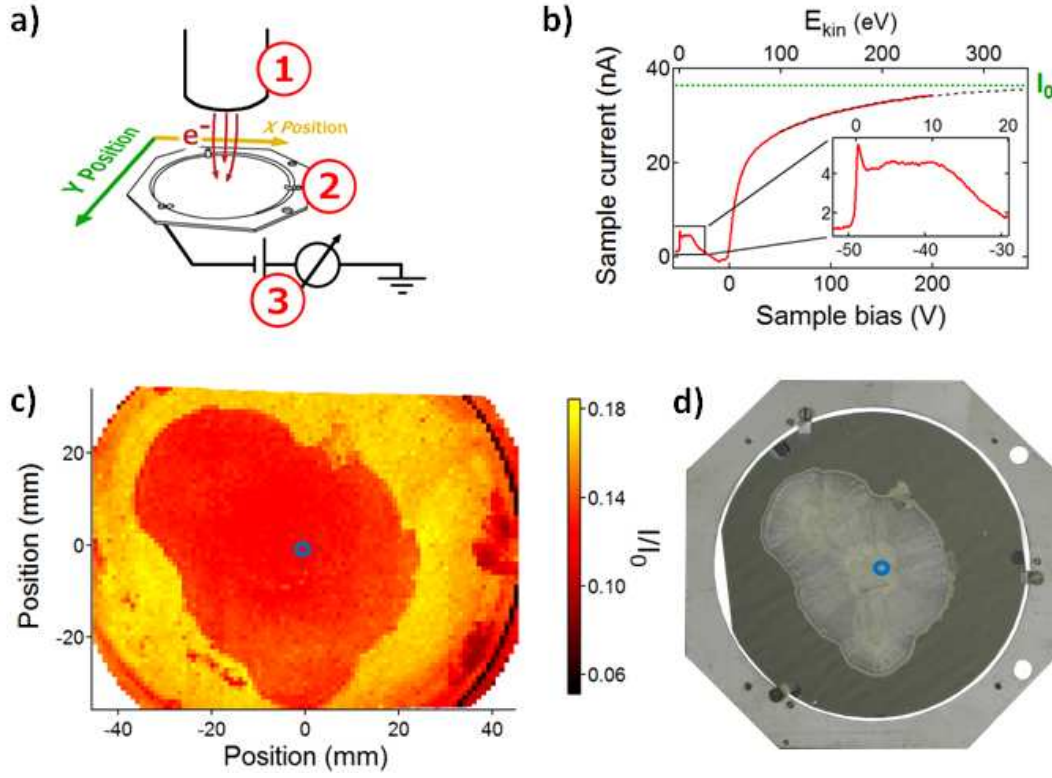


FIG. 2. Overview of the 4" wafer scale in-situ analysis capabilities. (a) shows the measurement scheme of the target current spectroscopy (TCS) setup. An electron source (1) provides electrons to probe the wafer (2). The electron energy is scanned via the sample bias (3) and a current-voltage spectrum for a 50 eV electron beam is shown in (b). The spectrum at low kinetic electron energies reveals the sample work function relative to the potential of the electron source and provides a finger print of the unoccupied sample states. At high electron energies, the spectrum is empirically extrapolated with an exponential function in order to estimate the total electron current (I_0). This is used for the determination of electron absorption (I/I_0) or reflection ($1-I/I_0$) for different electron energies. (c) is a 5 eV electron energy absorption image of an Ir(111) wafer with a melted gold patch as contrast. The absorption ranges from 6 to 18 % and is larger for iridium than for gold. The spacial resolution is 1 mm and each data point contains a complete TCS measurement –the spectrum in (b) is the data set from $(X,Y) = (0,0)$, the position indicated by the blue circle. A photograph of this wafer and its holder is shown in (d).

with borazine (HBNH_3) as a precursor at a substrate temperature above 750°C .⁶ The success of the preparation depends on the single crystallinity of the substrate, the cleanliness of the substrate and the low pressure at elevated sample temperature. These three requirements are crucial for many UHV/CVD processes and thus, similar performance can be expected for other deposition procedures. The monolayer of *h*-BN on Rh(111) allows in air transfer for sequential analysis or experiments. It forms a 3.2 nm honeycomb superstructure, which can be detected by different characterization methods (LEED, UPS or STM) and hence, grants access to a comprehensive picture of the BN-layer quality⁶.

The substrate is a single crystalline Rh(111) film, which is grown on a Si(111) wafer with an yttria-stabilized zirconia (YSZ) buffer layer⁷. The silicon wafer provides an inexpensive basis, which is available with high quality and fits industrial standards. The mosaic spread of the oxide buffer layer is typically higher than 1° . Nevertheless, heteroepitaxial metal films with excellent alignment, i.e. an angular spread of $0.1 - 0.3^\circ$, can be obtained by applying a two-step growth process as described in by Gsell *et al.*⁷. Under these conditions, a certain minimum thickness is required before the initially isolated metal islands growing in Volmer-Weber mode coalesce and form a closed film. A thickness of 150 nm has been found as a good compromise to achieve a closed flat film. Rhodium, like many other transition metals, can react with silicon to form eutectic mixtures with strongly reduced melting points. In the case of copper thin films, this process is not suppressed by a YSZ buffer layer⁹. For Ir/YSZ/Si(111) it was recently reported that an increase of the YSZ film thickness from several ten to 100 nm guaranteed a stability of the whole layer system under graphene growth conditions above 1000°C ¹⁰. In the present experiments, XPS investigations exclude decomposition or silicon diffusion to the Rh surface for a 50 nm thick YSZ buffer layer and a one hour temperature exposure to 850°C . Besides the usual steps at the edges of growth terraces, the epitaxial metal films show a large number of straight lines due to mono atomic steps. Their alignment is along three symmetry equivalent directions, which are visible in the STM images in Figure 4a)b). We attribute them to slip lines caused by the plastic relaxation of strain that is induced by every temperature change due to differences in the coefficients of thermal expansion (CTE's) between the metal film and the substrate. Despite these slide lines, Rh X-ray photoelectron diffraction (XPD) investigations on previously annealed and prepared samples indicate the conservation of the of the Rh(111) orientation.

A single atomic layer deposition is sensitive to any surface contamination and defects

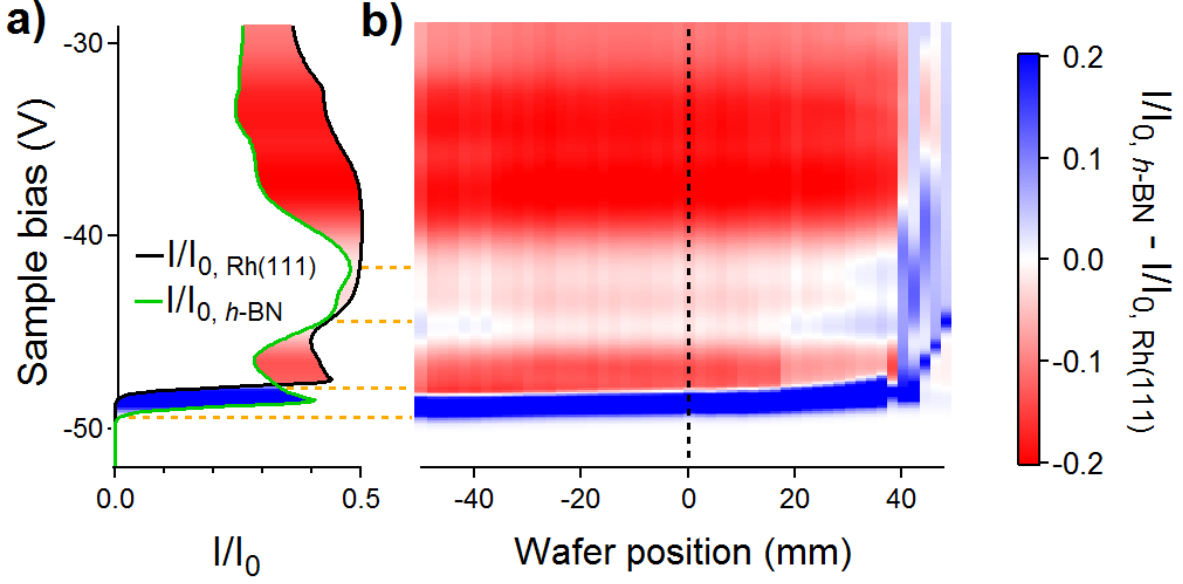


FIG. 3. Target current measurements on the $Y = 0$, $X = \pm 45$ mm wafer cross section before and after $h\text{-BN}$ preparation. The incident electron energy is 50 eV. (a) displays the measured data at the position $(X, Y) = (0, 0)$. It is the electron absorption for the pristine $\text{Rh}(111)$, $I/I_{\text{total}, \text{Rh}(111)}$ and the electron absorption for the system $h\text{-BN}/\text{Rh}(111)$, $I/I_{\text{total}, h\text{-BN}/\text{Rh}(111)}$. The dotted lines are guides to the eye. The data in (b) show the difference between the pristine $\text{Rh}(111)$ and the $h\text{-BN}/\text{Rh}(111)$ across the complete $Y = 0$ wafer cross section. A larger electron absorption before the BN coating is coded in red and a smaller electron absorption in blue. The red part indicates a reduction of sample current caused by the single layer of $h\text{-BN}$. The blue, 1.4 eV broad stripe reveals a work function lowering along the complete wafer. The uniformity of the measurement indicates a complete and homogeneous boron nitride growth on the 4" wafer, except for spectra with $X \geq 40$ mm, the edge of the wafer and its Mo fixation induce a retarding field distortion (see Figure 2d)). The measurements were performed without intermittent air exposure or cutting.

and thus, preceding the $h\text{-BN}$ preparation, a thorough cleaning procedure is necessary. Carbon is the main contamination of the surface and an incomplete cleaning leads to the formation of graphene structures¹¹, which form –upon borazine exposure– BN-graphene heterostructures¹². A complete cleaning procedure includes an isopropanol ultrasonic bath, followed by in-situ O_2 plasma cleaning, Ar sputtering and a 13 hours degassing up to $\sim 600^\circ\text{C}$. The preparation consists of 4 oxygen dosing cycles at increasingly higher temperatures, ranging from 600°C to 740°C , with subsequent flashing to 850°C . The amount of oxygen

applied, was related to the carbon partial pressure, which is monitored simultaneously by a quadrupole mass spectrometer. For the BN layer, 675 Langmuir ($1 \text{ L} = 1 \text{ sec} \cdot 10^{-6} \text{ Torr}$) of borazine was applied at pressures of $5 \times 10^{-7} \text{ mbar}$, while the substrate is kept at 820°C with a base pressure of $3 \times 10^{-9} \text{ mbar}$.

The preparation has been analyzed in-situ with normal incidence target current spectroscopy. Figure 3 visualizes two measurements series before and after the CVD boron nitride preparation. They reveal a homogenous electron absorption across the entire wafer and their comparison indicates a homogeneous change of the surface across the wafer. The work function decreased in the order of 1.4 eV, which is expected for the *h*-BN preparation on rhodium^{13,14} and the electron reflectivity is enhanced. To complete the quality control, the wafer was cut into smaller samples, some of which were transferred for further analysis into another UHV system¹⁵. Figure 4 displays STM images, UPS and LEED measurements of 5 different samples from the same wafer. All methods confirm the high quality of the boron nitride monolayer, regarding its regularity measured by the LEED, its electronic structure investigated by UPS and the corrugation, which was mapped by STM.

IV. CONCLUSIONS

A 4 inch wafer preparation setup for UHV/CVD processes is introduced. The application potential of the system is proven by the successful preparation of a single layer hexagonal boron nitride on a Rh(111) single crystalline thin film. The quality of the BN monolayer is comparable to the highest quality achieved with bulk Rh single crystals. In contrast to bulk single crystals, the single crystalline thin film approach supplies inexpensive and large area coatings. The setup is universal and can be used for many other UHV processes, where large area samples are required, e.g. for CVD graphene. The application of the latest generation thin film wafers with a YSZ buffer layer of 120 nm promise CVD processes up to 1000°C ¹⁰.

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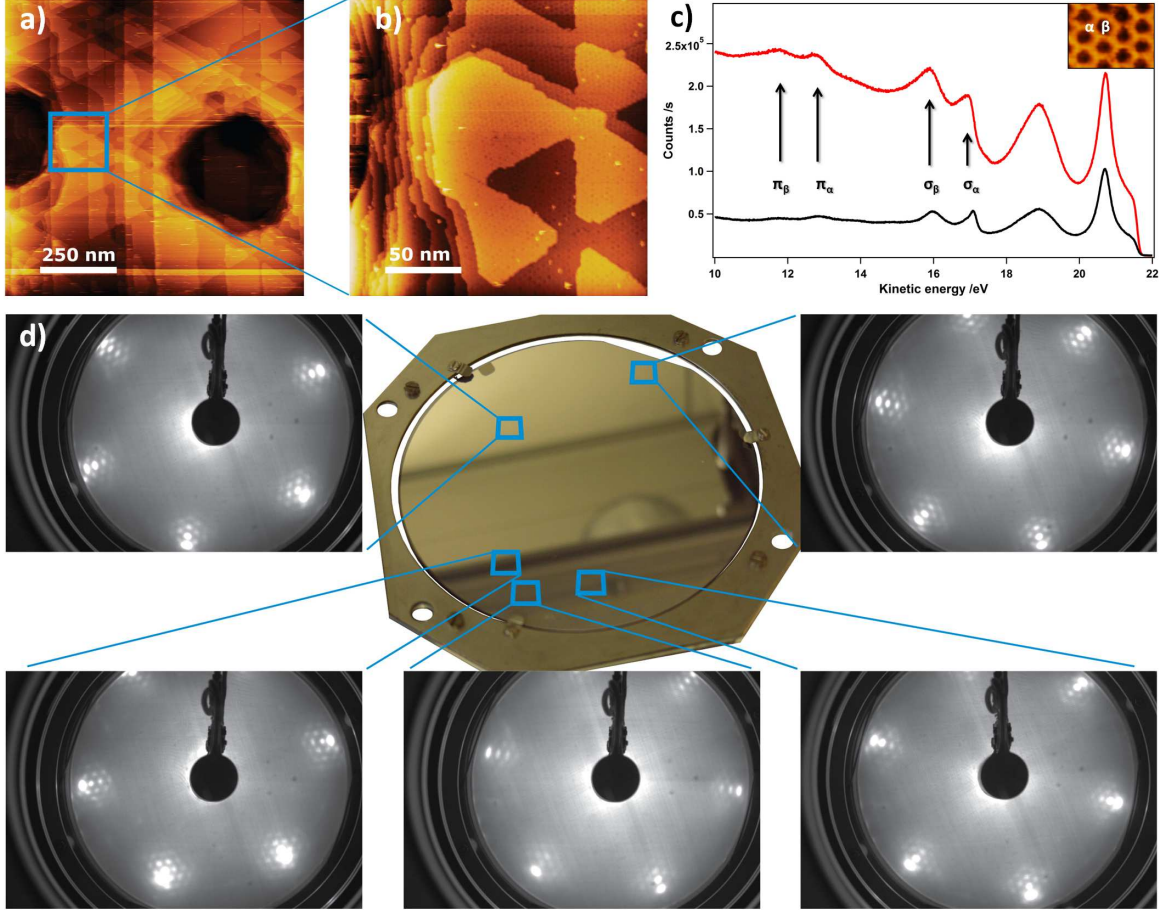


FIG. 4. Room temperature $1\mu\text{m} \times 1\mu\text{m}$ STM image (a), which resolves the threefold geometry of the rhodium film substrate and shows hole like features with the size of about $0.25\ \mu\text{m}^2$ and a depth in the range of 5 nm. The $200\text{nm} \times 200\text{nm}$ STM image in (b) indicates a complete *h*-BN layer by mapping its corrugation within the complete field of view. The STM scanning parameters for both images are $U_t = 1.0\ \text{V}$, $I_t = 0.5\ \text{nA}$. (c) Normal emission UPS spectrum of a thin film *h*-BN/Rh(111) sample (red) with the one prepared on a single crystal substrate (black). The splitting of the σ and π bands of the boron nitride layer are confirmed and assigned to the two distinct binding regions α and β as shown in the up-right corner image. (d) LEED patterns at 65 eV kinetic energy on different wafer positions. The superstructure forms a regular pattern around the first order spots of Rh, which only appear for successful BN-preparations. The wafer is cut into small samples, in order to use a common LEED unit, STM and photoemission spectrometer.